Studies on Electrolytic Titanium from Fused Salts

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Kenji ONO, Tomoo MATSUSHIMA, Kyoshû HATA
and Tsunakichi KURIYAMA

The Reseach Institute of Mineral Dressing and Metallurgy

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Synopsis

In this report, the authors studied the electrolytic production of titanium from fused salts.

At first, the authors determined the phase diagrams of some electrolytes of binary or ternary fused salts chiefly composed of K_2TiF_6. By further experiments, the solubility of TiO_2 in these salts was determined.

Then, the mechanism of electrolysis was studied by the measurement of the decomposition voltage of TiO_2 in fused salt, and the result was discussed by thermadynamic study.

Part 1. On the melting point of some fused salts

I. Introduction

Nowadays industrial production of titanium is done by "Kroll" process[1] by magnesium reduction of titanium tetrachloride. From the viewpoint of purity, the product from the decomposition of titanium iodide is excellent, but the production on a large scale under this method is not easy. On the other hand, many studies[2]~[4] have been done on the production of electrolytic titanium from fused salts. Although this last attempt has not yet been established on an electrolytic basis because of some incomprehensible behaviors of the electrolytic production and further for its industrial application.

From this point of view, the authors studied some electrolytes of binary and ternary fused salts chiefly composed of K_2TiF_6, and the solubility of TiO_2 in these salts.

II. Thermal decomposition of K_2TiF_6

K_2TiF_6 was easily prepared from alkaline double fluoride of titanium, but it was observed to decompose at high temperature.

The evolution of TiF_4 from the solid state was described. Then, the authors observed its decomposition stage by the use of thermal balance.

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* The 84th Report of the Research Institute of Mineral Dressing and Metallurgy.

(1) J. W. Kroll: Trans. Electrochem. Soc. **78** (1940), 35.
(2) S. Okamoto: Institute of Metals (Japan) **14** (1937), 46.
(3) A. Brenner and S. Senderoff: J. Electrochem. Soc. **99** (1952), 223.
(4) G. D. P. Cordner and H.W.Worner: Australian J. Appl. Sci. **2** (1951), 358.

0.4~0.5 g of the sample was accurately weighed and heated from room temperature to 800°C at the rate of 5°C/min. under normal atmospheric condition. During the heting the observed weight loss rapidly increased at about 300°C and changed slowly at about 500°C to 800°C as in Fig. 1.

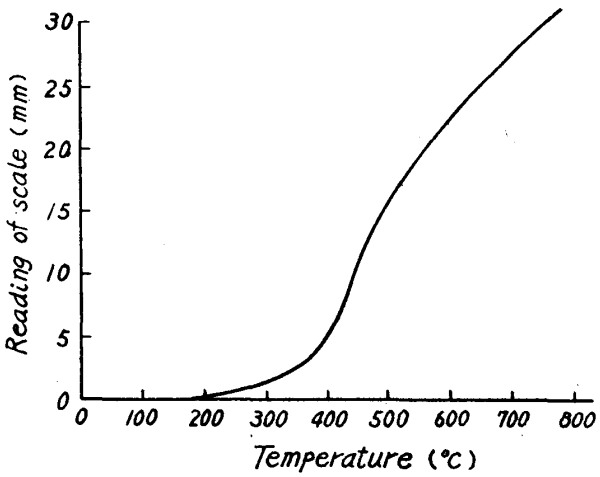

Fig. 1. Thermal decomposition of K_2TiF_6.

Under a dry atmospheric condition, Ginsberg[5] observed the formation of K_2TiOF_4 at 500°C, where the reaction was illustrated as follows:

$$2K_2TiF_6 + O_2 = 2K_2TiOF_4 + 2F_2 \qquad (1)$$

If the reaction is based on the above equation (1), the calculated weight loss is to be 9.16 per cent at 500°C, while the value is about 14 per cent at the same temperature in Fig. 1. This fact can not be represented by equation (1).

If K_2TiF_6 is easily decomposed by H_2O at high temperature, the following reaction should be considered:

$$K_2TiF_6 + 2H_2O = TiO_2 + 2KF + 4HF \qquad (2)$$

This reaction shows 18.32 per cent of weight loss in K_2TiF_6. In Fig. 1, about 18 per cent of weight loss is observed at 800°C. After experiments no loss of titanium could be recognized by chemical analysis. This result shows no evolution of TiF_4 and the formation of K_2TiOF_4, when the reaction is considered to proceed according to equation (2) by the effect of moisture in the atmosphere.

III. The binary system of K_2TiF_6 and alkali chlorides

As mentioned above, the decomposition of K_2TiF_6 at high temperature could not be prevented in the presence of moisture, and the composition of its melt was changed and its fluidity decreased.

To prevent these changes, it was considered better to dilute it by alkali chlorides for the purpose of decreasing the melting point of K_2TiF_6.

The experiments were done as follows: Mixtures of various compositions of K_2TiF_6 and alkali chlorides were melted down in a 20 cc platinum crucible. An electrolytic furnace was used as the heating source.

When the mixture of salts was transparently dissolved at constant temperature, it was cooled at the rate of 15~20°C/min. The cooling time and temperature were measured. The temperature was read by a calibrated Pt·Pt-Rh thermocouple.

(5) H. Ginsberg.: Z. anorg. u. allgem. Chem. **201** (1931), 193.

The experimental results are summarized in Figs. 2 and 3, representing the results shown in Tables 1 and 2.

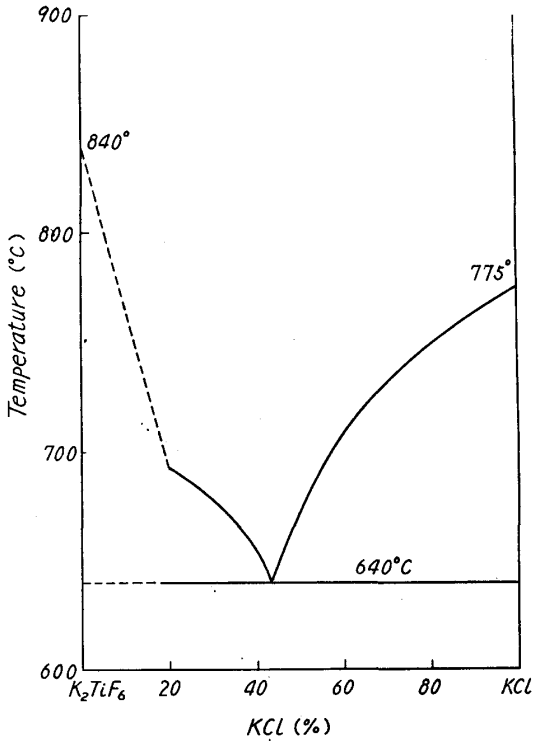

Fig. 2. The binary system of K_2TiF_6–KCl.

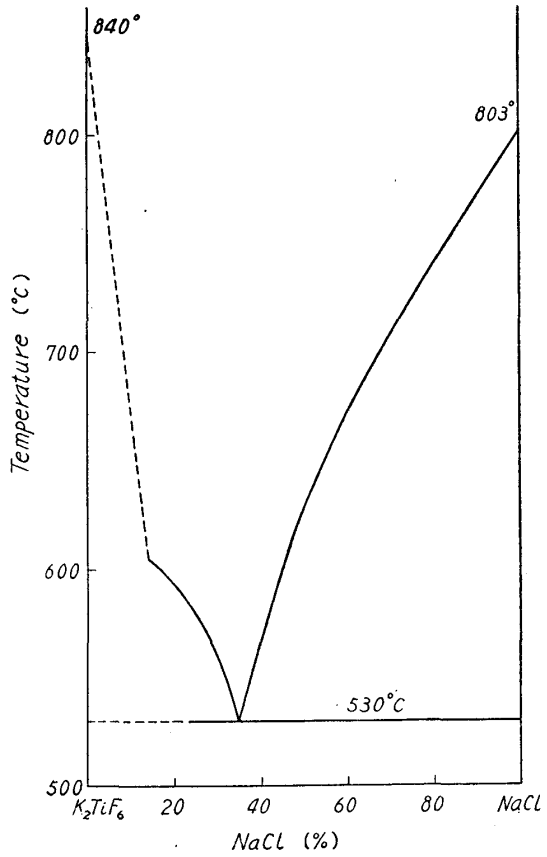

Fig. 3. The binary system of K_2TiF_6–NaCl.

Table 1. The system of K_2TiF_6–KCl.

Composition (%)		Melting Point
K_2TiF_6	KCl	(°C)
100	0	840
90	10	684
80	20	690
70	30	682
60	40	652
50	50	670
40	60	710
30	70	732
20	80	745
10	90	755
0	100	775

Table 2. The system of K_2TiF_6–NaCl.

Composition (%)		Melting Point
K_2TiF_6	NaCl	(°C)
100	0	840
90	10	610
80	20	595
70	30	560
60	40	565
50	50	631
40	60	671
30	70	708
20	80	740
10	90	771
0	100	803

At higher concentration of K_2TiF_6 and higher temperature, the measurement was difficult because of the proceeding of the decomposition of K_2TiF_6. In a long melting at high temperature, the mixture was colored violet-blue, and the product was difficult to dissolve in acids.

IV. Ternary system of K_2TiF_6–NaCl–KCl

Lowering the melting point of fused salts was effective in supressing the

Table 3. The system of K_2TiF_6–KCl–NaCl.

Composition (%)			Melting Point
K_2TiF_6	KCl	NaCl	(°C)
80	4	16	620
,,	8	12	640
,,	12	8	655
,,	16	4	675
70	9	21	590
,,	15	15	610
,,	21	9	641
65	3.5	31.5	541
,,	7	28	552
,,	10.5	24.5	561
,,	14	21	593
60	4	36	546
,,	8	32	541
,,	12	28	550
,,	16	24	566
,,	20	20	583
,,	24	16	592
,,	32	8	627
55	4.5	41.5	582
,,	9	36	550
,,	13.5	31.5	553
,,	18	27	567
,,	22.5	22.5	580
,,	27	18	593
50	5	45	599
,,	10	40	585
,,	15	35	577
,,	20	30	577
,,	25	25	585
,,	30	20	598
,,	40	10	625
45	5.5	49.5	619
,,	11	44	592
,,	16.5	38.5	590
,,	22	33	585
,,	27.5	27.5	593
40	6	54	632
,,	12	48	612
,,	18	42	596
,,	24	36	595
,,	30	30	606
,,	36	24	617
,,	48	12	662
30	14	56	660
,,	28	42	620
,,	42	28	628
,,	56	14	678
20	16	64	676
,,	32	48	630
,,	48	32	640
,,	56	24	660
,,	64	16	690

decomposition of K_2TiF_6. When this was recognized in the binary system, in which the eutectic point was 200~300°C lower than the melting point of K_2TiF_6, the melting point of the ternary systems was measured.

The results with the system of K_2TiF_6-NaCl-KCl are summarized in Table 3. The isothermal lines are drawn in Fig. 4 within the error of ±8°C. This shows that the eutectic point of K_2TiF_6-NaCl is the lowest point.

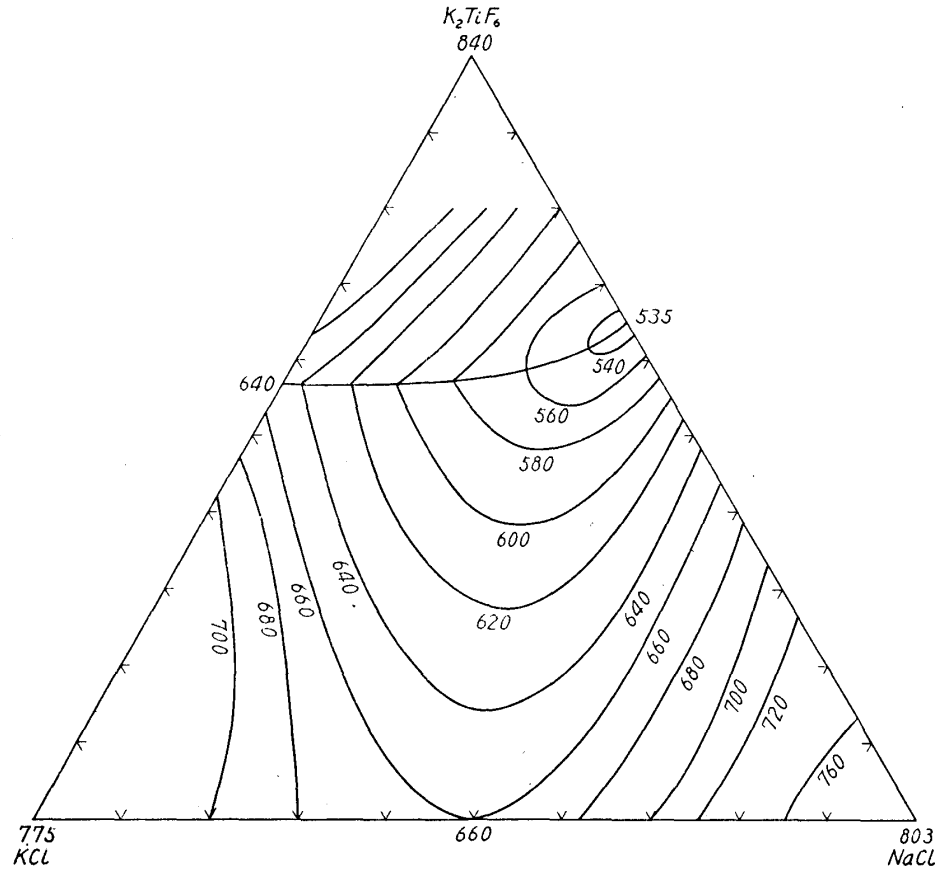

Fig. 4. The isothermal line of the melting point of the ternary system of K_2TiF_6-KCl-NaCl.

V. The system of K_2TiF_6 and alkali fluorides

In the systems of K_2TiF_6-KF and -NaF, the decomposition of K_2TiF_6 was more or less prevented in the range between the eutectic point and its lower concentration.

In this range, the melting point from the heating and cooling curves were almost in agrreement. The melting point was increased in rich K_2TiF_6 side while repeated measurements caused decomposition of K_2TiF_6. The observed values are found in Tables 4 and 5. Figs. 5 and 6 show the diagrams of the system.

In the binary salts of K_2TiF_6-KF, the eutectic point was 710°C and its composition was 65 per cent K_2TiF_6, and also the peritectic reaction was considered to be present in the rich K_2TiF_6 side, from the observed halting point of the cooling curve.

Table 4. The system of K_2TiF_6–KF.

K_2TiF_6 (%)	Primary Crystallization Point (°C)	Eutectic Point (°C)	Peritectic Point (°C)
0	850 847		
10	832 840		
20	806 820	701 710	
30	800 800	700 710	
40	767 770	710 710	
50	752 754	703 712	
60	719 720	710 710	
70	725 730	710 712	
75	739 741	698 703	
80	752 760	700 710	
85	770 785		749 751
90	795 800		746 748
95	808 811		731 730
100	850 845		

Table 5. The system of K_2TiF_6–NaF.

K_2TiF_6 (%)	Primary Crystallization Point (°C)	Eutectic Point (°C)
20	940 951	
30	925 925	648 660
40	895 899	640
50	872 880	688
60	842	642
70	795	660
75	790 798	650
85	700 709	650
90	690 700	660 660
92	651 642	—
95	729 732	650
97	754 762	660
100	850 842	

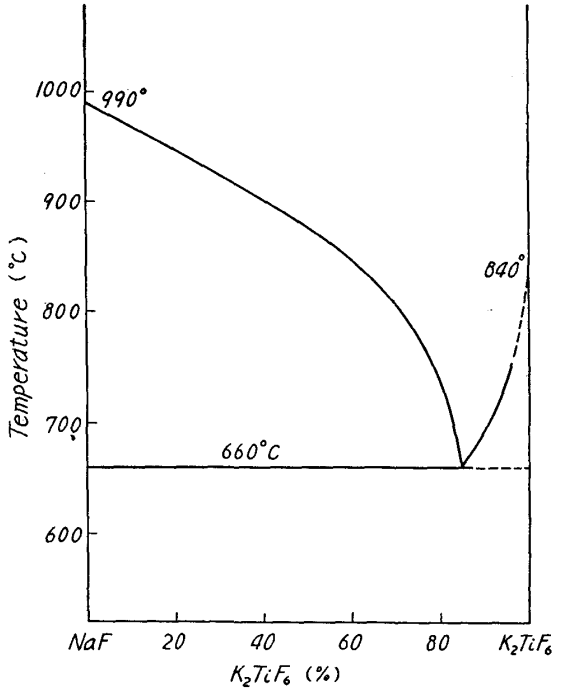

Fig. 5. The binary system of K_2TiF_6–NaF.

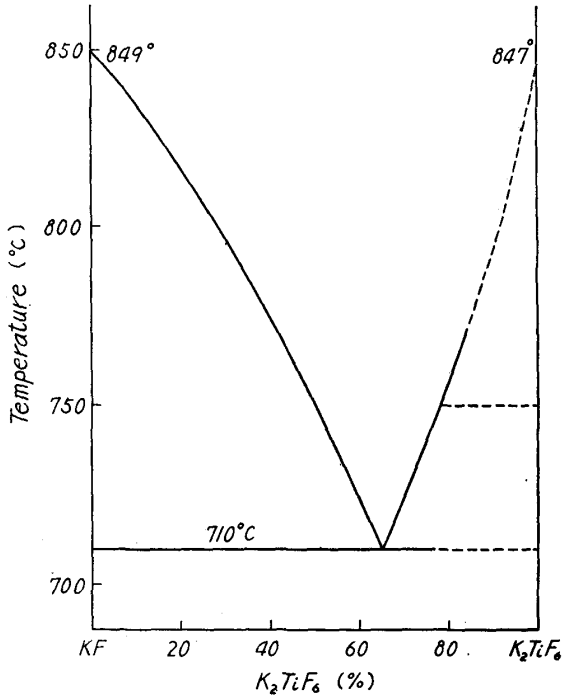

Fig. 6. The binary system of K_2TiF_6–KF.

The eutectic point of the binary salts of K_2TiF_6–NaCl was observed at 660°C and 87 per cent K_2TiF_6. The decomposition of K_2TiF_6 in this system was smaller than that of K_2TiF_6. The decomposition of K_2TiF_6 in this system was smaller than that of K_2TiF_6–KF. This was considered to be the reason for the lower eutectic temperature.

VI. The system of K_2TiF_6–NaCl–TiO_2

The solubility of TiO_2 in the binary salts of K_2TiF_6–NaCl was measured by thermal analysis. When TiO_2 was dissolved in fused salts within the range of concentration of 30~70 per cent NaCl, evolution of gas occurred. The solubility of TiO_2 was about 3.3 per cent and no considerable change in the melting point was observed. A long heating of the salts in molten state raised the melting temperature.

Blue residue remained in the bottom of the crucible from salts containing 5.5 per cent of TiO_2. But the melting temperature corresponded to the results of the cooling curve of the lower concentration of TiO_2. Then, the melt was not transparent. This was considered to be due to the saturation of the melt by TiO_2. This estimation of the solubility of TiO_2 shows that 3 per cent TiO_2 is soluble in the observed range summarized in Table 6.

Table 6. The system of K_2TiF_6–NaCl–TiO_2.

Composition (%)		Melting point (°C)			Primary halting point (°C)
K_2TiF_6	NaCl	TiO_2 : 0%	TiO_2 : 1.1%	TiO_2 : 3.3%	TiO_2 : 5.5%
70	30	560	553	551	548
65	35	535	530	526	547
60	40	565	—	553	—
50	50	631	618	610	615
40	60	671	677	669	665
30	70	708	713	712	703

VII. The system of K_2TiF_6–NaF–TiO_2

TiO_2 is the most soluble in this system, but it behaves as if it were in the system of K_2TiF_6–NaCl. The maximum concentration of the transparent melt was considered to be 5 per cent TiO_2. The isothermal line of the melting point is found in Fig. 7.

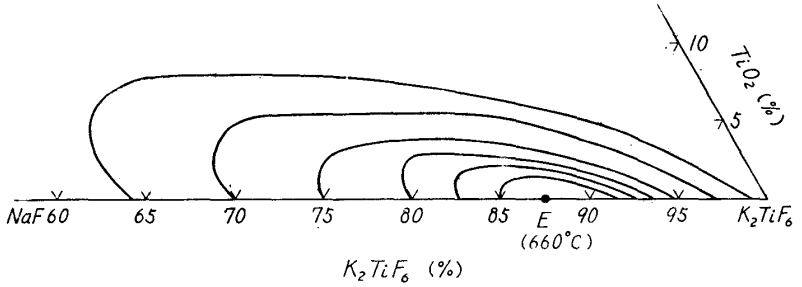

Fig. 7. The isothermal line of the melting point of the ternary system of K_2TiF_6–NaF–TiO_2.

Summary

Experiments were carried out to determine the melting points of binary or ternary fused salts chiefly composed of K_2TiF_6 and the solubility of TiO_2 in the fused salts.

(1) In alkali double fluorides of titanium, K_2TiF_6 was prepared easily, but the decomposition of this compound at high temperature could not be prevented in the presence of moisture.

(2) The eutectic points of binary systems were determined as follows:

System	K_2TiF_6–NaCl	K_2TiF_6–KCl	K_2TiF_6–NaF	K_2TiF_6–KF
Temp. (°C)	535	640	660	710
K_2TiF_6 (%)	65	57	85	65

(3) About 3 per cent of TiO_2 was soluble in fused K_2TiF_6–NaCl in the range from 30 to 70 per cent NaCl.

(4) About 5 per cent of TiO_2 was soluble in fused K_2TiF_6–NaF and the melting point of fused salt rose as the quantity of TiO_2 increased.

Part 2. On the mechanism of electrolysis

I. Introduction

In the previous work, the authors determined the melting point of the binary systems of the fused salts such as K_2TiF_6–NaCl, K_2TiF_6–KCl, K_2TiF_6–KF. By further experiments, the solubility of titanium dioxide in fused K_2TiF_6-alkalihalide systems was determined. The results obtained showed that the existing range of soluble titanium dioxide suggests the possibility of the electrolytic production of metallic titanium in the same manner as the electrometallurgy of alumina in cryolite. In producing metallic titanium by electrolysis from its fused fluoride, no continuous process is accompanied by the increased concentration of KF in the case of electrolvtes such as K_2TiF_6, as shown in the previous reports[6][7].

On the other hand, continuous procedure was carried out in the electrolysis of titanium monoxide in calcium chloride bath[8].

From this point of view, the authors studied the mechanism of electrolysis of titanium dioxide in fused salts. A measurement of the decomposiotion voltage was made and the electrode reaction were explained from thermodynamic consideration to illustrate the results.

(6) M. A. Steinberg, S. S. Calton, M. E. Sibert and E. Wainer: J. Electrochem. Soc. **102** (1955), 332.

(7) P. Drossbach: Z. Elektrochem. **57** (1953), 548.

(8) M. E. Sibert, Q. H. McKenna, M. A. Steinberg and E. Wainer: J. Electrochem. Soc. **102** (1955), 252.

II. Measurement of the decomposition voltage

The decomposition voltage was measured by the neutral electrode method. The details of the procedures are found in technical notes[9][10].

The modification of the apparatus is shown in Fig. 8. As the cathode, the anode and the neutral electrode platinum wire of 0.5 mmϕ were used. The distance between electrodes was 1 cm, and the depth to which they were dipped in the salts was 1 cm. In these experiments the maximum concentration of K_2TiF_6 was 40 per cent in the binary salts of K_2TiF_6–KF to prevent any considerable decomposition of K_2TiF_6 which was observable in its higher concentration in atmosphere.

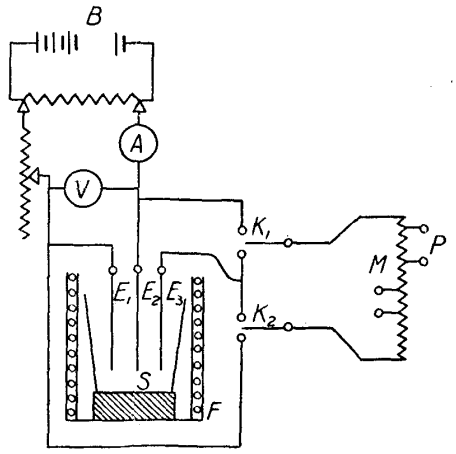

Fig. 8. Experimental Apparatus.

A	Ampere meter	K_1, K_2	Switch
B	Battery	M	Magnifier
E_1	Cathode	P	to Potentiometer
E_2	Anode	S	Fused Salt
E_3	Neutral Electrode	V	Volt meter
F	Electric Furnace		

15 gm of the sample was held in a platinum crucible, the salt containing TiO_2 were melted down at a constant temperature, the electrodes were dipped and the electric potential and the current of coupled E_1–E_2 and E_2–E_3 were measured. After complete melting of the salts and TiO_2, the time required for measurement was 5 minutes. During the increasing of the voltage, evolution of gas was observed and the cathode surface began to be covered by deposition of a black material.

The cathode was almost completely covered by the black deposit near the second-break-point in the figure, showing the relation between the electric potential and the current. The results are shown in Figs. 9~11 by measurements versus temperatures. These figures identically show that two break-points exist in the neiborhood of 0.8~0.9 V and 1.7~1.8 V, but these points proved

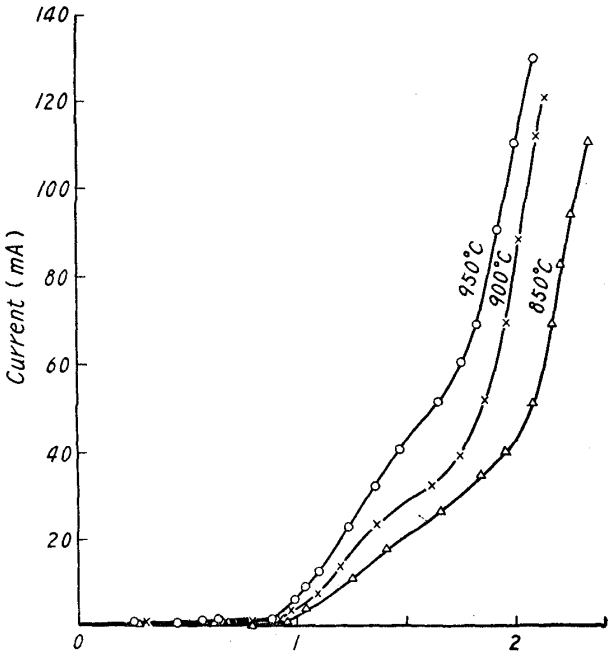

Fig. 9. Decomposition voltage (20% K_2TiF_6–3% TiO_2).

(9) T. Takei: Jitsuken Denkikagaku (Experimental Electrochemistry) (1941), 182.
(10) Y. Katô, K. Funaki and K. Inoue: J. Electrochem. Soc (Japan) **4** (1936) 137.

to fall to the side of the lower voltage at higher temperature. Throughout the measurements, the difference in concentration of TiO_2 in the fused salts had no effects on the decomposition voltage at constant temperature. This fact should be considered as illustrating that the increased concentration of TiO_2 produced by decomposition of K_2TiF_6 has no effect under the normal atmospheric condition.

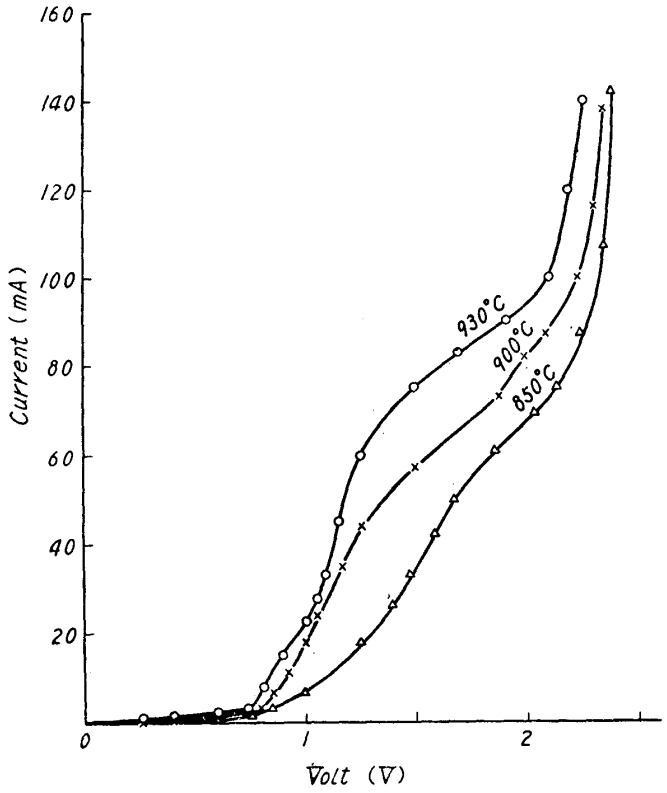

Fig. 10. Decomposition voltage ($30\%K_2TiF_6$–$3\%TiO_2$).

The effect of small quantities of water in fused salts was pointed out by H. Shinohara et al[11]. In order to see this effect, the result of polarization of both electrodes is shown in Fig. 12. The polarization is very small in the anode side as a result of the evolution of gas, but it is recognized near the first break-point of the cathode side which accompanies

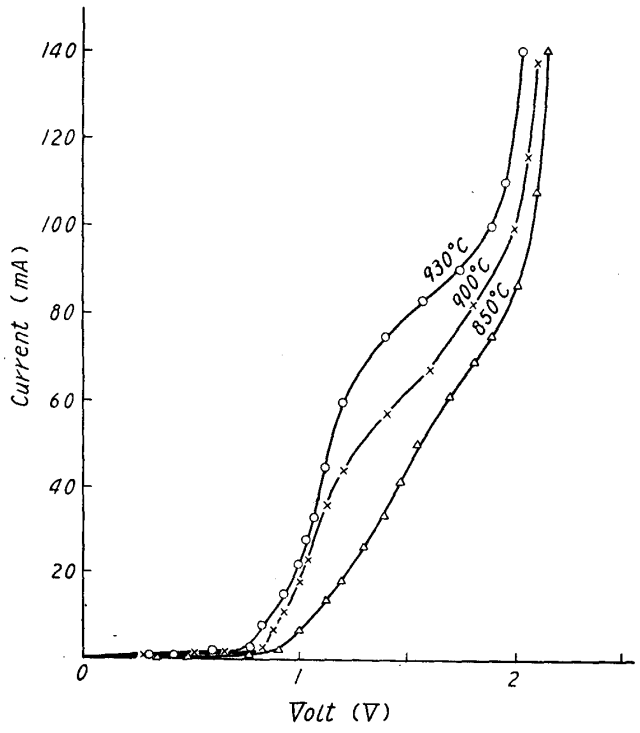

Fig. 11. Decomposition voltage ($40\%K_2TiF_6$–$3\%TiO_2$).

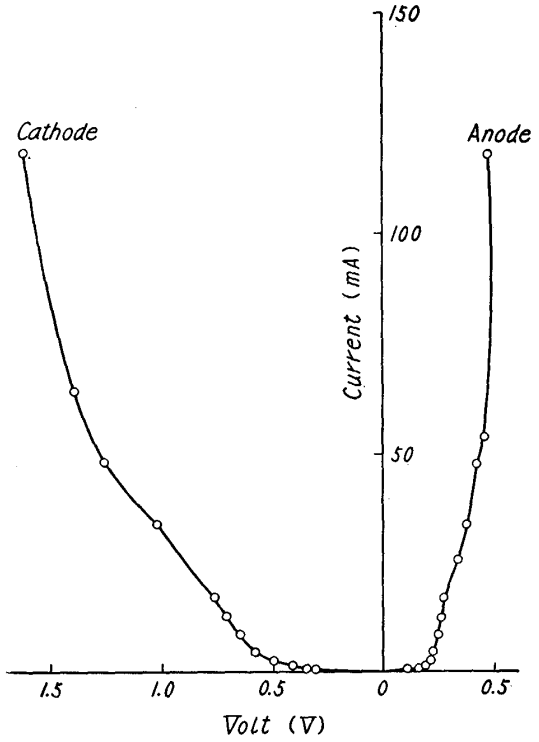

Fig. 12. Polarization of anode and Cathode.

(11) H. Shinohara, W. Sakai and T. Okuno: J. Electrochem. Soc. (Japan) **10** (1942), 16.

the deposition. This fact shows no effect of H_2O in the authors' experiments.

III. Consideration

The two observed values of the decomposition voltage are compared with the mechanism of the electrolytic reaction.

Drossbach[3] measured the decomposition voltage of the system of LiCl-KCl-K_2TiF_6 by the graphite electrodes at 600°C. He considered the reaction to be as follows, from which the values 1.5V was obtained:

$$K_2TiF_6 + C = 2KF + Ti + CF_4 \quad (1)$$

Also the depolarization value of CF_4 formation was calculated from the thermodynamic data to be 1.4 V at 600°C.

From these results, the decomposition voltage is about 3.0 V, corresponding to the following equation:

$$K_2TiF_6 = 2KF + Ti + 2F_2 \quad (2)$$

With a similar experiment, Steinberg[6] obtained the value 1.8 V at 809°C from the fused salts of K_2TiF_6 and NaCl with graphite electrodes. At the same temperature the depolarization voltage of CF_4 formation was 1.36 V. Then the corresponding value was 3.2 V in equation (2).

A fair agreement is seen in order of the two values.

Nasu[12] reported the free energies of formation of suboxide of Ti_2O_3 from TiO_2 as follows:

$$2TiO = Ti_2O_3 + 1/2\,O_2 \quad (3)$$

$$\Delta F^\circ = 61{,}250 - 4.1769T\log T - 0.005506T^2 - 37.10\cdot10^{-8}T^3 + 6.13T \quad (4)$$

When Sibert[8] obtained TiO from the reaction between TiC and ZnO at high temperature, he measured the decomposition voltage of TiO in $CaCl_2$ bath. Drossbach[13] calculated the decomposition voltage of various oxide of titanium. Also the free energies of the reaction of the dissociation

Table 7. Theoretical decomposition voltage.

E (V) / Temperature (°K)	E_1 $Ti/TiO_2/O_2$	E_2 $Ti_2O_3/TiO_2/O_2$
900	1.90	1.10
1,000	1.84	1.07
1,100	1.80	1.02
1,200	1.74	0.97

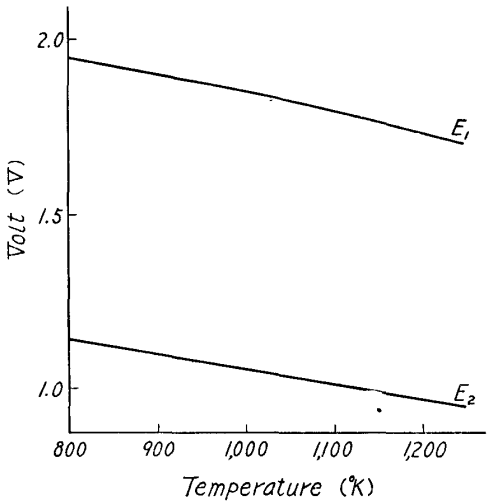

Fig. 13. Relation between theoretical decomposition voltage and temperature.

(12) N. Nasu: Sci. Repts. Tôhoku Univ. 1st Ser., **25** (1936), 510.
(13) P. Drossbach: Z. Elektrochem. **59** (1955), 512.

of TiO_2 was calculated from thermodynamic data[14] as follows:

$$TiO_{2(rutil)} = Ti_{(\beta)} + 1/2O_2 \qquad (5)$$

$$\Delta F^\circ = 216{,}554 + 7.62T\log T - 0.72\cdot10^{-3}T^2 + 1.78\cdot10^5T^{-2} - 58.41T \qquad (6)$$

From these results, the theoretical values of the decomposition voltage are calculated in Table 7 from equations (4) and (6) and $\Delta F_T = -nFE_T$, which are represented in Fig. 13.

On the other hand, the decomposition voltage of KF was about 4.5 V at 900°C as follows:

$$2KF = 2K + F_2 \qquad (7)$$

The authors' results showed that TiO_2 was decomposed in fused salts of K_2TiF_6–KF. It is suggested that the first break-point was caused by the equation (3), and the second break-point was based on the formation of Ti from TiO_2.

Summary

Two break-points were recognized in the measurements of the decomposition voltage of the system of K_2TiF_6, KF and TiO_2.

The cathode deposit was dark black and it was not metallic.

This was inferred from the reaction of the formation of Ti_2O_3 and Ti. It was considered that the electrolytic deposition of metallic tiatnium in the system was not possible because of the formation of suboxide.

(14) K.K. Kelley: U.S. Bureau of Mines Bull. **476** (1949), 192.